FC

Textile Research Institute
Princeton, New Jersey

Technical Report No. 16

to

The Office of Naval Research

on

Contract No. Nonr-09000 and Nonr-09001

Effect of Drawing on the Infra-Red Dichroism of Nylon 66 Filaments

by

Gino Caroti and Joseph H. Dusenbury

30 April 1956

EFFECT OF DRAWING ON THE INFRA-RED DICHROISM OF NYLON 66 FILAMENTS

by

Gino Caroti[#] and Joseph H. Dusenbury[*]

ABSTRACT

Infra-red absorption measurements in the 3-micron region, using polarized radiation, have been made for a series of nylon 66 filaments, ranging in draw ratio from one (undrawn) to four. From consideration of the dichroic ratios obtained, it is suggested that there is a random arrangement of nylon 66 polymer chains at draw ratio one, with these chains becoming increasingly aligned with respect to the filament axis as the drawing increases. The method used to prepare a filament for infra-red examination is particularly important, since it has been found that improper preparative procedures may induce orientation in a filament. This effect of specimen preparation is greatest at draw ratio one and becomes less important at higher draw ratios. The results of x-ray diffraction studies carried out on the same series of filaments are consistent with the infra-red findings.

[#]Visiting Fellow, Textile Research Institute. Present address: Stazione Sperimentale Per I Combustibili, Milan, Italy.

[*]Assistant Director of Research, Textile Research Institute.

INTRODUCTION

If a high-polymeric material is to be used as a textile fiber, it is well known that the polymer molecules usually must be oriented in a direction generally parallel to the fiber axis. This is accomplished, in the case of nylon, by drawing out initially unoriented fibers at a temperature well below the melting point. The initially unoriented material is prepared by melt spinning. Nylon fibers exhibit crystallinity prior to cold drawing, and the crystallites change their orientation distribution from a random one, in undrawn fibers, to ones where the crystallites become increasingly oriented with respect to the fiber axis as drawing progresses. The corresponding changes in the fiber x-ray diffraction patterns have been described by Fankuchen and Mark [1].

As would be expected, many other properties of nylon fibers are also affected by the cold-drawing operation. Changes in birefringence have been reported by Munden and Palmer [2] and by Quynn [3]. Munden and Palmer also described how cold drawing modifies the dye-uptake characteristics of nylon. Speakman and Saville [4] have measured the effects of drawing on moisture sorption and swelling tendencies. Abbott and Goodings [5] have reported similar measurements and, in addition, have shown that the drawing operation produces only a slight increase in fiber density. Similar findings regarding density were reported prior to those of Abbott and Goodings by Black and Dole [6]. The effect of drawing on the elastic moduli of nylon 66 filaments

has been described by Wakelin, Voong, Montgomery, and Dusenbury [7].

Infra-red absorption measurements, using polarized radiation, provide another means of determining the orientation of the polymer molecules in a fiber. The effect of drawing on the infra-red dichroism of nylon 66 filaments has been reported by Quynn and Steele [3, 8]. These workers found that the four absorption bands they studied in the 3-micron region exhibited parallel dichroism at low draw ratios and, as drawing progressed, switched to exhibiting perpendicular dichroism. At a draw ratio of 2.99, the 3310 $cm.^{-1}$ absorption band (N-H stretching) was found to show parallel dichroism, whereas the band at 3075 $cm.^{-1}$ (presumably N-H stretching also) exhibited perpendicular dichroism. It is desirable that a picture of what drawing does to the arrangement of polymer chains in nylon filaments be consistent with x-ray diffraction [1, 3], birefringence [2, 3], and mechanical property measurements [7]. Since we have found it difficult, when the data of Quynn and Steele [8] are considered, to develop such a consistent picture of the drawing process, we have reinvestigated the effect of drawing on the infra-red dichroism of nylon 66 filaments.

In any determinations of the infra-red absorption spectra of chemical substances, the preparation of the sample for infra-red examination is of prime importance. In the case of the studies to be reported of the polarized infra-red spectra of variously drawn nylon 66 filaments, we have found that the method used for specimen preparation may have an important influence on the experimental results.

INFRA-RED STUDIES

The optics of the 0.78 N.A. reflecting microscope used, in connection with a Perkin-Elmer Model 12-C infra-red spectrometer equipped with a LiF prism, were identical with those of the instrument mentioned by Quynn and Steele [3, 8]. It was found possible to reduce the difficulties of focusing the Schwarzschild mirror pairs and adjusting the specimen stage by mounting these optics on a conventional light microscope base in a way similar to that used by Blout, Bird, and Grey [9]. A photograph showing the relative size of the modified microscope attachment used for the experiments reported here appears in Figure 1. A set of AgCl sheets was used to analyze polarized radiation transmitted through the specimen.

A series of nylon 66 filaments, which were prepared by melt spinning and ranged in draw ratio from one (undrawn) to four, was kindly supplied by E. I. du Pont de Nemours and Company. The undrawn filaments had a diameter of about 120 microns, which decreased with drawing to about 65 microns at draw ratio four, or at each draw ratio the filaments were approximately twice the diameter of those used by Quynn and Steele [8] and by Wakelin et al [7]. Specimens approximately 4 to 6 microns in thickness were found suitable for infra-red examination, and these were prepared by microtoming. The absorption bands of nylon are so intense in the 3-micron region, where the experiments were carried out, that dichroic ratios calculated for specimens of 12 microns or greater thickness have little quantitative significance.

Fig. 1. Photograph showing relative size of modified infra-red microscope attachment.

It is possible to obtain desirably thin specimens by mechanical flattening of single filaments as well as by longitudinal sectioning with a microtome. But it has been found in this work that the flattening process can induce orientation in a filament and that this effect is accentuated when the filament is of initially low orientation. Such induced orientation may be greatly reduced when longitudinal sections are prepared by microtoming filaments embedded in a plastic. The embedding medium used in this work was plasticized polymethylmethacrylate. A prior partial polymerization served in some instances to prevent excessive diffusion of monomeric methyl methacrylate into the nylon and subsequent swelling of the filaments. Infra-red examination of specimens, where diffusion of monomer had occurred and where it had been prevented, indicated that no altering of dichroic behavior had been caused by the embedding medium under the conditions used for the experiments.

All of the suitably thin longitudinal sections of nylon were prepared by microtoming plastic-embedded filaments. Three different methods of specimen preparation were used: (a) microtoming previously flattened samples with the direction of blade motion parallel to the filament axis, (b) microtoming undeformed samples in a direction perpendicular to the filament axis, and (c) microtoming undeformed samples in a direction parallel to the filament axis.

Another problem associated with microspectroscopic examination of fibers in the infra-red region is that of delusive energy or "stray light". When only the nylon filament is located at the specimen stage of the reflecting microscope, it

is found that a significant portion of the energy transmitted to the thermocouple of the spectrometer is energy which has gone around the edges of the filament and has become part of the filament image at the entrance slit of the monochrometer. At any given absorption band, accordingly, the apparent transmittance consists of light which has actually passed through the specimen plus stray light which has gone around it and added to the actual transmittance. The presence of such stray light may be easily demonstrated by placing at the specimen stage a metallic wire whose lateral dimensions are comparable with those of the filament being examined [10]. In the experiments reported here the stray light was masked out at the specimen stage by placing pieces of thin aluminum foil, with slits 30 to 70 microns wide depending on the specimen width, over the longitudinal sections of filaments.

In Figure 2 are shown the infra-red absorption spectra of undrawn filaments of nylon 66 and nylon 610. The nylon 610 samples were supplied by E. I. du Pont de Nemours and Company. These spectra are shown as they were obtained with the single-beam spectrometer, and the proper precautions were taken in regard to specimen thickness and the elimination of stray light. The direction of microtoming was parallel to the filament axis in these instances. It should be noted that the absorption due to N-H stretching at 3310 $cm.^{-1}$ (compare with the methylene group stretching motion at 2925 $cm.^{-1}$) is relatively greater in the case of nylon 66. This is not surprising, since nylon 66, a copolymer of hexamethylenediamine and adipic acid, contains one N-H group per five CH_2 groups in the polymer chains, whereas

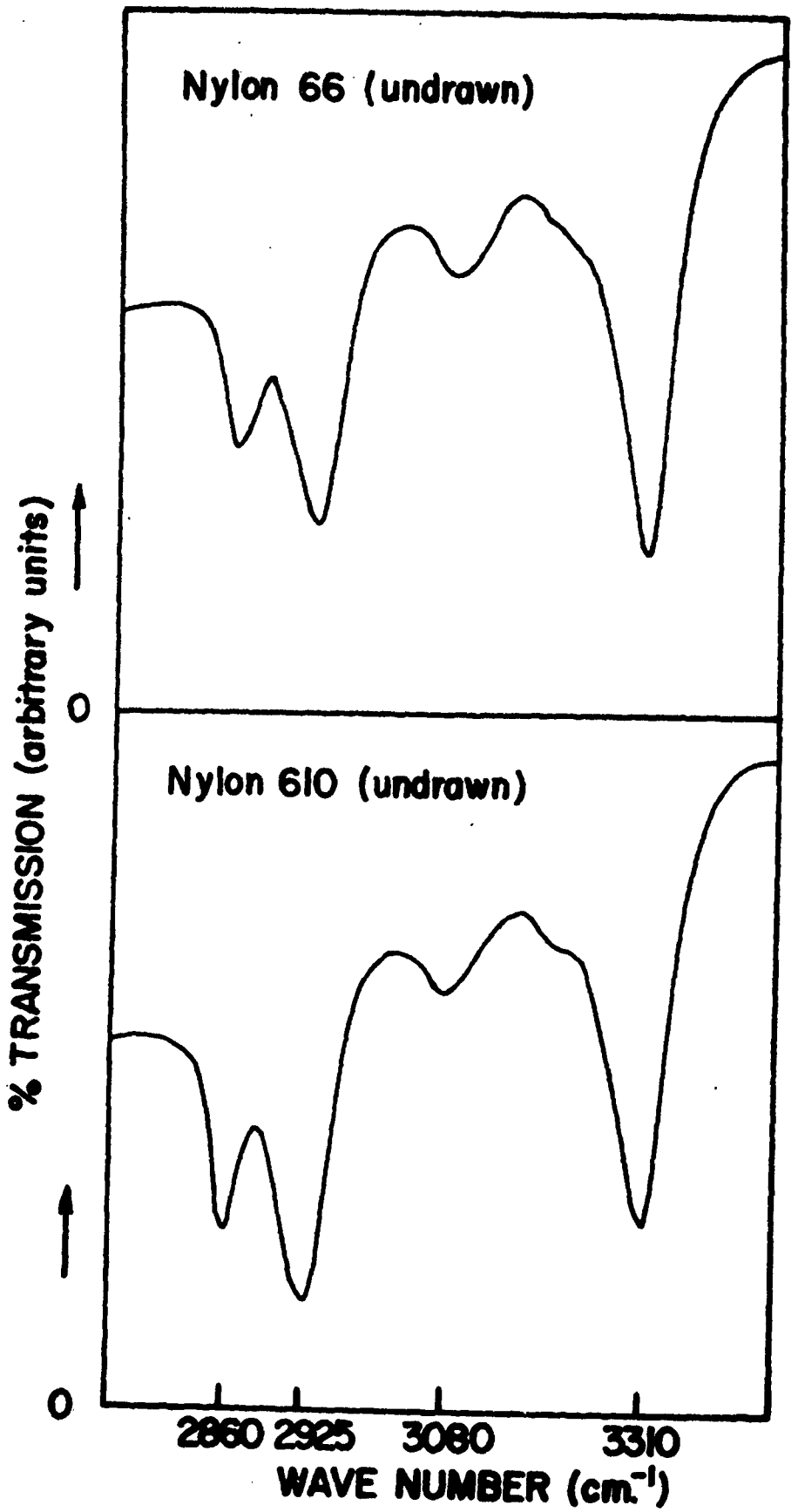


Fig. 2. Infra-red absorption spectra of single filaments of nylons 66 and 610.

nylon 610, a copolymer of hexamethylenediamine and sebacic acid, has one N-H group for every seven CH_2 groups. In connection with the experiments reported here, this relatively greater absorption of the N-H group in nylon 66 was used as a diagnostic tool for determining whether the specimens had been prepared properly for infra-red examination.

The consequences of improper preparative procedures are illustrated in Figure 3. Again the spectra are shown as originally obtained with the spectrometer. In this instance, polarized spectra of a nylon 66 filament at draw ratio four are shown, and it may be seen that a combination of too thick a filament and stray light leads to the calculation of incorrect dichroic ratios. When the stray light is present, for example, it is obvious that the apparent dichroism of the N-H stretching band at 3310 $cm.^{-1}$ is considerably less than that of the N-H stretching band at 3080 $cm.^{-1}$ and that, in general, the apparent absorption bands are considerably broader and more poorly defined than when proper procedures are used (Figure 2). When the stray light is eliminated, as shown also in Figure 3, the dichroic ratios calculable from the data indicate a greater extent of perpendicular dichroism, but the specimen is so thick that the absorption has increased to the point where the calculated dichroic ratios, with the possible exception of that for the 3080 $cm.^{-1}$ band, have dubious quantitative value. It is also apparent that the extent of absorption of the 3310 $cm.^{-1}$ band, when compared with that of the 2925 $cm.^{-1}$, is not as great as it should be for a nylon 66 filament. This point was discussed earlier in connection with the spectra shown in Figure 2. When the proper specimen preparation techniques were used, it was

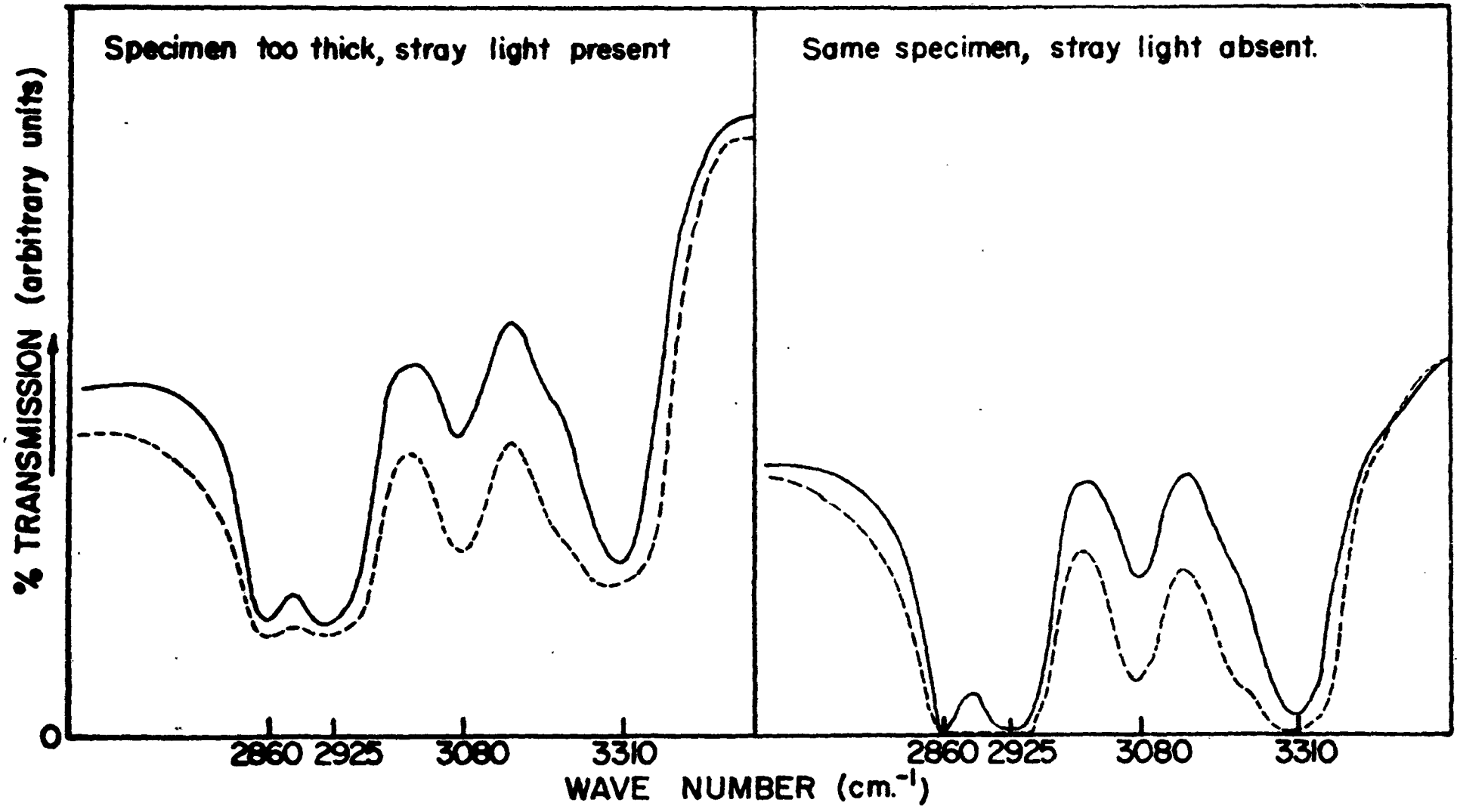


Fig. 3. Polarized infra-red absorption spectra of a nylon 66 filament at draw ratio 4 (solid line—with electric vector parallel to filament axis; dashed line—with electric vector perpendicular to filament axis).

found that the extent of absorption of the 3310 $cm.^{-1}$ band was appropriately increased over that shown in Figure 3 and that all of the absorption bands became more sharply defined and resembled those shown in Figure 2.

The dichroic ratios obtained from the polarized infrared spectra of properly prepared filament specimens are listed in Table I and plotted in Figure 4. In calculations of these ratios, allowance has been made for the reduction of energy caused by scattering at the sample, but no correction has been made for the effect of beam convergence in the reflecting microscope. It may be shown, using an analysis of the type described by Fraser [11], that the latter effect is a small one. Generally, the mean values shown in Table I are for measurements made on 5 to 14 filaments. In the cases of part (a) of Table I at draw ratio three and of parts (b) and (c) at draw ratio four, however, only two filaments were studied, and it is for this reason that the corresponding 95% confidence levels are relatively large.

When appropriate statistical consideration is given the data of Table I, it is observed that the effect of specimen preparation is greatest at draw ratio one and becomes less important at the higher draw ratios. Flattening induces considerable parallel dichroism of all the four absorption bands at draw ratio one, and this effect is much greater than that caused by microtoming plastic-embedded filaments in a direction perpendicular to the filament axis. Some perpendicular dichroism appears to be induced at draw ratio one when the microtoming is done in a direction parallel to the filament axis.

TABLE I

Dichroic Ratio ($\varepsilon_{\pi}/\varepsilon_{\sigma}$) Values for Nylon 66 Filaments*

$cm.^{-1}$	draw ratio 1.0	2.0	3.0	4.0
(a) microtoming previously flattened samples in direction parallel to filament axis				
3310	2.39±0.20	0.88±0.13	0.79±0.26	---
3080	2.35 0.17	0.90 0.11	0.78 0.52	---
2925	1.37 0.06	0.94 0.07	0.90 0.36	---
2860	1.58 0.06	0.92 0.07	0.89 0.04	---
(b) microtoming undeformed samples in direction perpendicular to filament axis				
3310	1.18±0.05	0.81±0.10	0.56±0.04	0.50±0.13
3080	1.14 0.04	0.77 0.07	0.61 0.08	0.54 0.13
2925	1.03 0.03	0.68 0.04	0.63 0.05	0.56 0.27
2860	1.06 0.03	0.81 0.05	0.68 0.03	0.66 0.43
(c) microtoming undeformed samples in direction parallel to filament axis				
3310	0.78±0.16	0.72±0.06	0.54±0.10	0.55±0.53
3080	0.78 0.16	0.67 0.03	0.52 0.05	0.45 0.35
2925	0.93 0.07	0.73 0.04	0.70 0.05	0.68 0.01
2860	0.85 0.10	0.78 0.04	0.70 0.04	0.65 0.43

*Limits shown are 95% confidence levels of the corresponding mean values.

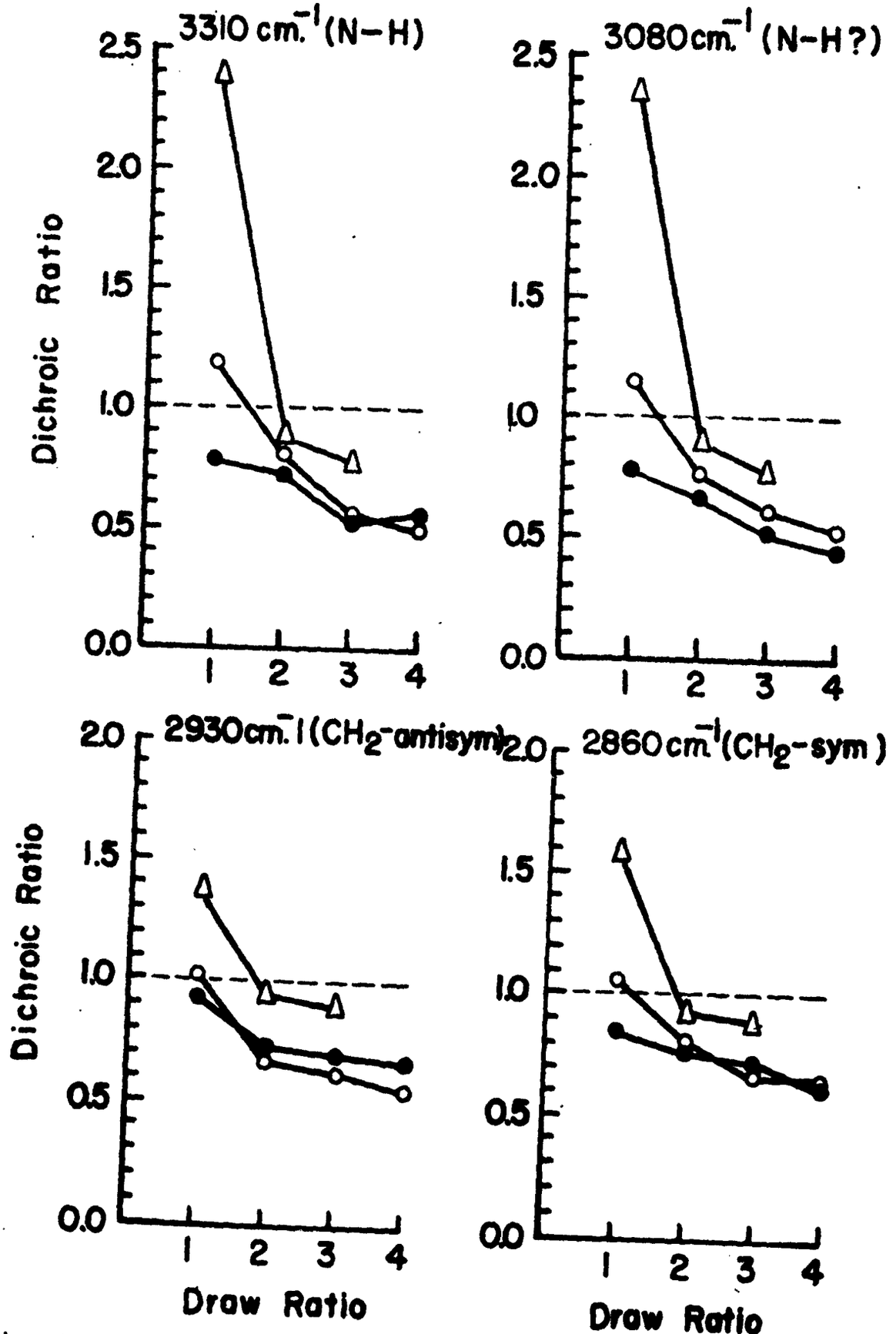


Fig. 4. Infra-red dichroism of nylon 66 filaments. Specimens prepared by microtoming: (Δ)--previously flattened samples in direction parallel to filament axis; (○)--undeformed samples in direction perpendicular to filament axis; (●)--undeformed samples in direction parallel to filament axis.

The dichroic behavior of the 3310 $cm.^{-1}$ band (N-H stretching) is identical with that of the 3080 $cm.^{-1}$ band (presumably N-H stretching). The two methylene group stretching motions at 2925 and 2860 $cm.^{-1}$ exhibit nearly the same dichroic behavior, and the extent of their dichroism is generally less than that of the two N-H stretching motions. With these filaments, there is no reversal of dichroic behavior in going from draw ratio two to higher draw ratios, as was observed by Quynn and Steele [8] whose data are shown plotted in Figure 5. The results listed in Table I and plotted in Figure 4 suggest a random arrangement of nylon polymer chains at draw ratio one, with these chains becoming increasingly aligned with respect to the filament axis as drawing progresses.

X-RAY STUDIES

Flat-plate x-ray diffraction patterns of bundles of nylon 66 filaments from the same draw ratio series have also been obtained. These patterns were taken with a North American Philips x-ray diffraction unit, using Ni-filtered Cu-Kα radiation and a specimen-to-film distance of 2.73 cm., and are shown in Figure 6.

From their x-ray diffraction measurements, Bunn and Garner [12] have worked out the crystal structures of both nylon 66 and nylon 610 and have shown that the density of nylon 66 crystals should be about 1.24. The densities for undrawn nylon 66 fibers of about 1.13 reported by Black and Dole [6]

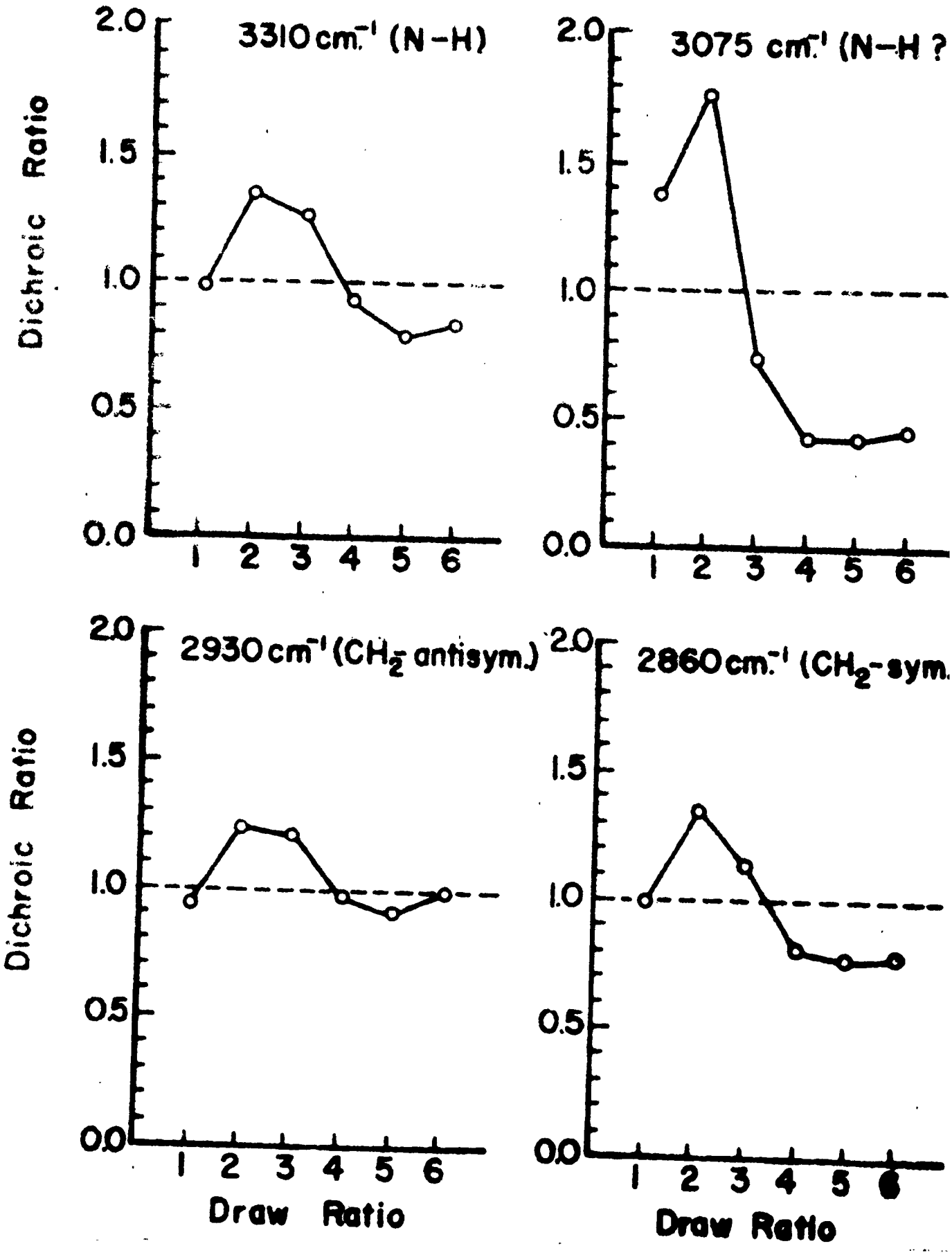


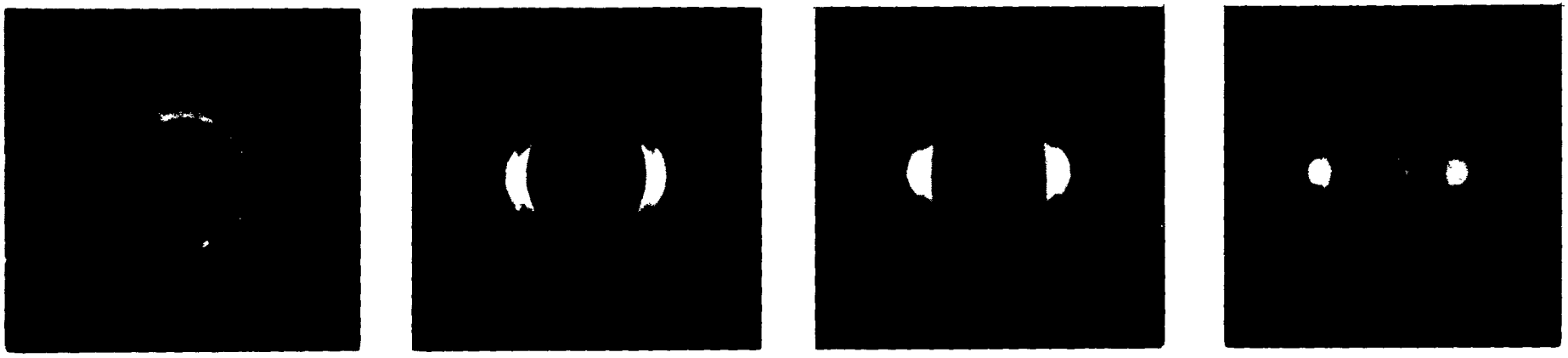
Fig. 5. Infra-red dichroism of nylon 66 filaments. Data of Quynn and Steele.

and of about 1.14 reported by Abbott and Goodings [5] indicate the presence of amorphous material with a lower density than that of the crystalline portions of the fibers. Since only slight increases in fiber density are caused by drawing [5, 6], it appears reasonable to suggest that the drawing process has little effect on the amount of crystalline material present. The x-ray diffraction patterns of unflattened filaments in Figure 6 lend qualitative support to this view and suggest that the effect of drawing is to orient the crystallites with respect to the filament axis. These findings are consistent with the infra-red dichroism measurements discussed earlier.

In addition, x-ray diffraction patterns have been obtained of mechanically flattened nylon 66 filaments at draw ratios one and two. These are also shown in Figure 6. It may be seen that orientation of crystallites in a direction perpendicular to the filament axis has been caused by flattening the undrawn nylon filaments. At both draw ratios one and two, there is evidence that the flattening has produced a double orientation of the crystallites which has been described by Bunn and Garner [12]. This effect is particularly noticeable when the x-ray diffraction pattern of flattened draw ratio two filaments (Figure 6, x-ray beam perpendicular to plane of the flattened filaments) is compared with the corresponding pattern for unflattened draw ratio two filaments. In the unflattened filaments, the strong, inner, equatorial arc, caused by reflection from the 100 planes of the nylon 66 crystallites, is comparable in intensity to the outer equatorial arc, caused jointly by reflections from the 010 and 110 planes, with the

UNFLATTENED FILAMENTS

d.r. 1 d.r. 2 d.r. 3 d.r. 4



FLATTENED FILAMENTS

d.r. 1 d.r. 2

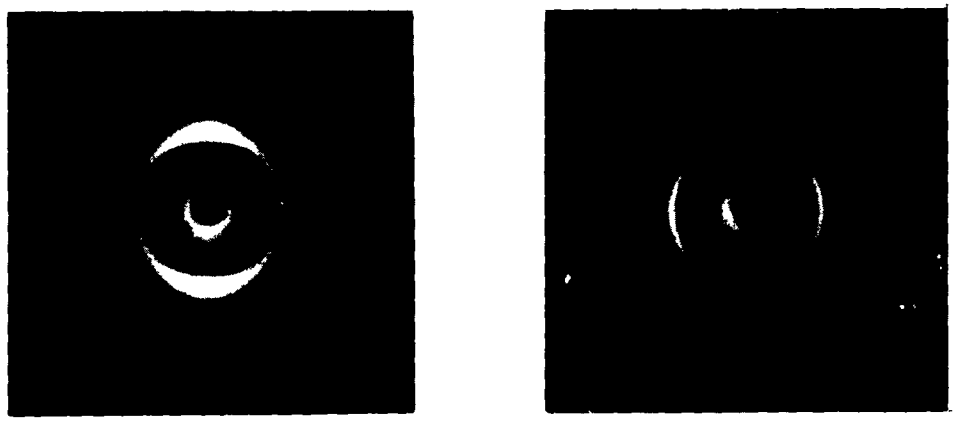


Fig. 6. X-ray diffraction patterns of nylon 66 filaments (↑ direction of filament axis).

010 reflection being the stronger. When these filaments are flattened (Figure 6), the intensity of the outer equatorial arc decreases greatly with respect to the inner one. This suggests that the 010 planes, in which the nylon polymer molecules are held together strongly by C=O•••H-N hydrogen bonds, have become oriented approximately in the plane of the flattened filaments. There is also some indication that the length of the inner equatorial arc has been increased by flattening, which suggests that the orientation of the 100 planes with respect to the filament axis may have been reduced. It is interesting that inspection of the diffraction patterns of the undeformed fibers reveals that drawing causes the outer ring to contract to equatorial arcs at an earlier stage than the inner one. This indicates that the 010 planes of the crystallites become oriented first, a finding similar to that first reported for nylon by Fankuchen and Mark [1].

These results for flattened filaments are in accord with the dichroic ratios observed for flattened nylon 66 filaments at draw ratios one and two (Table I and Figure 4). The results suggest, further, that the parallel dichroism found for the four nylon absorption bands at the lower draw ratios by Quynn and Steele [8] (Figure 5) may have been caused by the mechanical flattening procedure they used to obtain specimens suitably thin for infra-red examination.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Dr. J. H. Dillon, Director of Textile Research Institute, for his help and encouragement during this work, to Dr. J. H. Wakelin, for his helpful discussions pertaining to it, and to Mrs. H. S. Virgin, for obtaining the x-ray diffraction patterns. They are also grateful to Dr. R. G. Scott of the Pioneering Research Division, Textile Fibers Department, E. I. du Pont de Nemours and Company, and to Mr. A. B. Coe of these laboratories, for their advice and assistance in regard to the microtoming problems associated with this work. The authors' thanks are also due Mr. H. F. Hume of the Nylon Research Division, Textile Fibers Department, E. I. du Pont de Nemours and Company, for supplying the nylon 66 and nylon 610 filaments, and Mr. F. D. Dexter of the Development Laboratories, Bakelite Company, Union Carbide and Carbon Corporation, for supplying the embedding plastic and plasticizer materials. This study was conducted under the sponsorship of the Office of Naval Research, Department of the Navy.

LITERATURE CITED

1. Fankuchen, I., and Mark, H., J. Appl. Phys., 15, 364 (1944).
2. Munden, A. R., and Palmer, H. J., J. Textile Inst., 41, P609 (1950).
3. Quynn, R. G., Ph.D. Thesis, Princeton University (December 1954).
4. Speakman, J. B., and Saville, A. K., J. Textile Inst., 37, P271 (1946).
5. Abbott, N. J., and Goodings, A. C., J. Textile Inst., 40, T232 (1949).
6. Black, C. E., III, and Dole, M., J. Polymer Sci., 3, 358 (1948).
7. Wakelin, J. H., Voong, E. T. L., Montgomery, D. J., and Dusenbury, J. H., J. Appl. Phys., 26, 786 (1955).
8. Quynn, R. G., and Steele, R., Nature, 173, 1240 (1954).
9. Blout, E. R., Bird, G. R., and Grey, D. S., J. Opt. Soc. Amer., 40, 304 (1950).
10. Coates, V. J., Offner, A., and Siegler, E. H., J. Opt. Soc. Amer., 43, 984 (1953).
11. Fraser, R. D. B., J. Chem. Phys., 21, 1511 (1953).
12. Bunn, C. W., and Garner, E. V., Proc. Roy. Soc. (London), A189, 39 (1947).